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**(54) Polymer coated metallic  
pigments**

(57) Metallic pigments for paints  
comprise metallic pigment particles  
e.g. aluminium flakes, coated with a  
polymer in the amount of 0.1 to 30  
parts by weight per 100 parts by  
weight of metallic pigment. The

polymer is formed from a monomer  
having at least one epoxy radical and  
polymerisable double bond, or from a  
mixture of said monomer and a  
comonomer having a polymerisable  
double bond, or said mixture at a  
temperature of 60—200°C in the  
presence of a polymerisation initiator.  
They may include a silicone  
compound.

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## SPECIFICATION

## Polymer-coated metallic pigments

The present invention relates to polymer-coated metallic pigments and, more particularly, to such pigments used to produce paints for electrostatic painting, water-based paints, and paints for plastics products. It also relates to a process for producing the pigments.

Metallic pigments have been widely used to prepare paints for construction materials, light electrical appliances, machinery, ships, vehicles, automobiles, etc. and to prepare inks for printing on paper and plastics materials. On the other hand, electrostatic painting, painting using water-based paints, and painting on plastics materials have been highlighted in recent years for better painting efficiency and pollution-free conditions.

However, the use of conventional metallic pigments for such new types of painting is attended by various problems. In electrostatic painting, because of the poor ability of conventional metallic pigments to withstand voltage, the application of the high voltage required for this type of painting causes heavy current leakage. Also, when used for water-based paints, conventional metallic pigments react with water during storage to produce hydrogen gas because of poor water resistance so that the paint loses its metallic lustre and blackens. With plastics painting, baking of the finish cannot be used because of the low heat resistance of the plastics to be painted and paint containing conventional metallic pigment cannot but be dried at low temperature, usually 50—60°C. This results in poor cohesion of the paint film and, particularly, in poor cohesion between the metallic pigment and the binder of the film in comparison with baked films, even if the most suitable combination of binder and organic solvent is selected. The metallic pigments usually used for plastics painting are in the form of flakes and they are normally coated with fatty acids. If conventional metallic pigments are used for plastics painting, they exhibit poor orientation uniformity and poor cohesion in the paint film because of their poor affinity for the binder. The property of preventing such problems is hereinafter referred to as peelproofness.

Another problem is that shock due to static electricity is sometimes felt when one touches a metallic coat on an apparatus containing a high voltage generator such as a TV set. The property of preventing such a phenomenon is hereinafter referred to as shockproofness.

Another requirement for plastics painting is touchproofness. This is related to the fact that the paint film is dried, not by baking, but at low temperatures. A fingerprint remains on the paint film and the touched portion becomes white. The cause for this phenomenon has not been fully established, but a microscopic examination shows that the metallic pigment, at the touched portion, corrodes and minute cracks appear in the binder. On a paint film having a good touchproofness, no fingerprint is left.

It is an object of the present invention to provide metallic pigments which alleviate the aforementioned problems and to provide a process for producing such pigments.

The present invention consists in a metallic pigment for paint comprising metallic pigment particles coated with a polymer in the amount of 0.1 to 30 parts by weight per 100 parts by weight of the metallic component in the metallic pigment particles.

The polymer is obtained by polymerizing a monomer (hereinafter referred to as "monomer A") having a polymerizable double bond and at least one epoxy radical, singly or with at least one comonomer (hereinafter referred to as "comonomer B") having a polymerizable double bond.

The metallic particles used in the present invention may be aluminium, copper, zinc, iron, nickel or their alloys. They are usually flaky in shape, but are not limited to that shape.

The monomer "A" may be selected from among epoxidated polybutadiene, glycidyl methacrylate, glycidyl acrylate, cyclohexenevinyl monoxide, divinylbenzene monoxide, etc.

The polymerizable comonomer "B" may be styrene,  $\alpha$ -methyl styrene, vinyl toluene, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl propionate, acrylic acid, acrylic ester, methacrylic acid, methacrylic ester, crotonic acid, itaconic acid, citraconic acid, oleic acid, maleic acid, maleic anhydride, divinylbenzene, etc.

Among acrylic esters which can be used, there are methyl acrylate, ethyl acrylate, n-butyl acrylate, 50 2-ethylhexyl acrylate, lauric acrylate, stearyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, methoxyethyl acrylate, butoxyethyl acrylate, cyclohexyl acrylate, 1,6-hexanediolacrylate, and 1,4-butanediolacrylate.

Among methacyclic esters which can be used, there are methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, 2-ethylhexyl methacrylate, lauric methacrylate, stearyl methacrylate, hydroxyethyl 55 methacrylate, hydroxypropyl methacrylate, methoxyethyl methacrylate, butoxyethyl methacrylate, and cyclohexyl methacrylate.

In accordance with the present invention, the coating of the metallic pigment particles with a polymer is performed by dissolving a monomer A or a mixture of a monomer A and a comonomer B in an organic solvent, dispersing the metallic particles in the solution, heating the reaction system to a predetermined temperature, and adding a polymerization initiator to start polymerization. By this process, a polymer is deposited on the metallic particles. After reaction, the metallic pigment thus coated is filtered, concentrated and separated from the reaction system.

As the organic solvent, mineral spirit is preferable. However, the following may also be used: aliphatic hydrocarbons, such as hexane, heptane, octane and cyclohexane; aromatic hydrocarbons, such

as benzene, toluene and xylene; halides, such as chlorobenzene, trichlorobenzene, trichloroethylene and tetrachloroethylene; alcohols, such as methyl alcohol, ethyl alcohol, n-propyl alcohol, n-butyl alcohol; ketones, such as 2-propanone and 2-butanone; esters, such as ethyl acetate and propyl acetate; and tetrahydrofuran, diethyl ester, and ethyl propyl ester.

5 As a polymerization initiator, organic peroxides such as di-t-butyl peroxide, acetyl peroxide, benzoyl peroxide, lauroyl peroxide, cumyl hydroperoxide, and t-butyl hydroperoxide, and azo compounds such as  $\alpha$ ,  $\alpha'$ -azo-bisisobutyronitrile may be used. But, the last-mentioned is the most preferable because it is pyrolyzed at relatively low temperatures.

The reaction temperature for polymerization may be 60—200°C. If  $\alpha$ ,  $\alpha'$ -azo-bisisobutyronitrile is used, it is 70—90°C. For lower or higher temperatures outside those ranges, the reaction speed or the polymerization efficiency decreases.

10 The polymerization should preferably be performed in an atmosphere of an inert gas, such as nitrogen, helium or argon for higher polymerization efficiency.

15 The amount of the polymer coated on the metallic pigment particles should be 0.1—30 parts by weight, preferably 0.5—15 parts by weight, per 100 parts by weight of the metallic component in the metallic pigment particles. For less than 0.1 part, the required advantages may not be obtained. For more than 30 parts, there is merely an increase in manufacturing costs without any substantial increase in performance or function.

20 The ratio by weight of the monomer A to the comonomer B is preferably 3:10 to 10:10 because such ratio gives the resulting polymer a higher crosslinking density, thus giving the final product the better performances required for use as a metallic pigment for paints.

25 In order to make the polymer-coated metallic pigment dispersible in water, a suitable amount (about 10—16 weight % with respect to the non-volatile component in the pigment) of a known surface active agent may be added thereto. The surface active agent may be either an anionic one, such as fatty acid soaps, long chained alcohol sulfate, polyoxyethylene alkyl ether sulfate, polyoxyethylene isoctylphenyl ether sulfonate, and alkyl benzene sulfate, or a nonionic one, such as polyoxyethylene alkyl ether, polyoxyethylene alkylphenol ether, polyoxyethylene alkylamide, polyoxyethylene fatty acid ester, polyoxyethylene sorbitan fatty acid ester, and sorbitan fatty acid ester.

30 If it is desired to provide good touchproofness to a paint film on a plastics material, a silicone compound may be added to the polymer-coated metallic pigment. Furthermore, its addition gives good wettability to the surface of the paint film, thus allowing it to be used for printing. The addition of a silicone compound may be effected by dissolving the silicone compound in a medium, such as mineral spirit, and diluting the solution and adding it to the polymer-coated pigment in an ordinary mixing step for adjusting the volatile to non-volatile ratio.

35 The amount of the additive may be 0.5—5.4 parts by weight per 100 parts by weight of the non-volatile component in the polymer-coated metallic pigment. For less than 0.5 parts, the touchproofness would be inadequate. For more than 5.4 parts, it would be adequate but the cost would be higher and the resulting paint film would not be suitable for printing.

40 If a metallic tone of colour is required in a paint film used for plastics painting, the amount of the polymer coated on the metallic pigment should be 0.5—3 parts by weight.

45 The silicone compound used in the present invention may be either a silicone oil or a silicone resin. The usable silicone oils include dimethyl polysiloxane, epoxy-modified silicone oil and carboxy-modified silicone oil. Any known silicone resin may be used.

50 A polymer-coated metallic pigment in accordance with the present invention shows different advantages for different amounts of polymer coating as follows:

If the amount of coating polymer on the metallic pigment is 1.5 parts by weight or more, preferably 3 parts or more, to 100 parts of the metallic component in the metallic pigment, the paint obtained has a good ability to withstand voltage and can be used for electrostatic painting.

55 If the amount of coating is 0.5 parts or more, preferably 1 part or more, the paint obtained exhibits a good water stability when used as a water-medium paint. This property may be checked by testing for the amount of gas generated and the change in colour tone.

If it is 0.1 parts or more, preferably 0.5 parts or more, the paint obtained exhibits a good peelproofness.

If it is 3 parts or more, preferably 7 parts or more, good shockproofness may be expected. If a silicone compound is added to the polymer-coated metallic pigment, good touchproofness is obtained.

In order further to illustrate the invention, reference will now be made to the following non-limiting examples. Unless otherwise stated, quantities are expressed in parts by weight.

**EXAMPLES 1—8**

60 One thousand grams of mineral spirit was put into a 2-litre four-neck flask. The monomer A or a combination of a monomer A and a comonomer B as shown in Table 1 were added thereto and agitated in the flask. (In the table, EPB, GMA, GA, 1.6—, and AA are abbreviations for epoxidized polybutadiene, glycidyl methacrylate, glycidyl acrylate, 1,6-hexanedioidiacrylate, and acrylic acid, respectively.) Aluminum flakes were added to the solution and agitated to disperse them uniformly. The aluminium flakes used were HS—2, 1200M and MG—1000, all manufactured by Toyo Aluminium Co.

Ltd. (In the Table, NV denotes the weight % of the non-volatile component contained therein.) The reaction system was heated to a predetermined temperature in a nitrogen gas atmosphere. One gram of  $\alpha,\alpha'$ -azobisisobutyronitrile was then added and the system was allowed to polymerize. The reaction temperature and reaction time are shown in the Table. After reaction, by filtering and concentrating the mixture, a polymer-coated aluminium pigment was obtained. The weight % of the non-volatile component (NV) in the resulting pigment is shown in the Table.

To determine the amount of polymer coating on the pigment, part of the pigment obtained was washed with n-hexane, filtered and powdered, and the metallic component in the pigment powder was dissolved off with a solution consisting of hydrochloric acid, nitric acid and water in the ratio by weight of 1:1:2. The polymer residue was filtered, dried and weighed. The amount of polymer coating is shown in the Table in parts by weight in relation to 100 parts of the non-volatile component in the polymer-coated pigment.

The pigment obtained was subjected to mixing by use of a mixer to adjust the percentage of the non-volatile component.

15 In Example 8, epoxy-modified silicone oil (SF—8411, manufactured by Toray Silicone Co.) was added as a silicone compound to the pigment and the mixture underwent mixing. In the Table, the amount of SF—8411 is shown in parts by weight per 100 parts of non-volatile component in the pigment. The percentage of the non-volatile component (NV) after the mixing is shown in the Table.

#### CONTROLS 1 and 2

20 Control 1 was aluminium pigment (HS—2, Toyo Aluminium Co. Ltd.), uncoated with polymer. Control 2 is the control 1 to which a silicone compound SF—8411 was added as in Example 8.

The polymer-coated pigments, after mixing, and the uncoated central pigments were tested in the following six tests. The results of the test are shown in the Table.

#### TEST 1

##### (Electrostatic painting Test)

From the pigments obtained, sample paints were prepared as follows: 80 parts of acryl varnish (Acrylic 47—712, manufactured by Japan Reichhold Chemicals Inc. NV 50%) and 20 parts of melamine (Super Beckamine J—820 of the same maker, NV 60%), both being binders, were mixed so that the metallic component in the pigment was 15 parts by weight per 100 parts of the solid component in the binder. The mixture was diluted with a solvent consisting of xylene, methyl isobutyl ketone and diacetone alcohol in the ratio by weight of 60:25:15 so that the viscosity measured with a Ford cup No. 4 was 12 seconds. The paint thus made was painted on tinplate by means of a Grooved Mini-Bell electrostatic painting device (manufactured by Ransburg Japan Ltd.) at a voltage of 90KV and at a paint supply rate of 200 cc per minute.

#### 35 TEST 2

##### (Gas Evolution Test)

3 grams of each sample metallic pigment (in terms of its metallic component) was dispersed in 100 grams of an aqueous medium consisting of water and butyl cellosolve in the ratio by weight of 1:4. The dispersion was kept at 50°C for 24 hours and the amount of gas given off from the dispersion was measured. It is shown in the Table in millilitres per one gram of the metallic component in the pigment.

#### TEST 3

##### (Colour Difference Test)

One hundred parts of each polymer-coated aluminium pigment was kneaded with 3 parts of polyoxyethylene alkylphenolether (Emalgen 906 of KaO Sekken Co.) 6 parts of polyoxyethylene alkylether (Emalgen 408 of KaO Sekken Co.). To 48 g of the water-dispersible aluminium pigment thus obtained were added and mixed, 90 g of distilled water, 560 g of water-soluble acryl varnish (Arolon 557N of Nisshou Arrow Chemical Co. NV 50%), 150 g of water-soluble melamine varnish (Sumimal M—50W of Sumitomo Chemical Co. Ltd., NV 78%), and 32 g of phthalocyanine blue (INK blue of Dainippon Ink Co.). The water-dispersible metallic paint thus obtained was kept at 50°C for one month. Before and after storage, portions of the paint were painted with a doctor blade on a test paper sheet and the difference  $\Delta E$  in colour was measured by the use of a differential colourimeter.

#### TEST 4

##### (Peelproofness Test)

To 100 g of acryl lacquer (Acrylic A—166 of Japan Reichhold Chemical Inc. NV 50%) was added 5 g (in terms of metallic component) of each aluminium pigment obtained. The mixture was diluted with a solvent consisting of toluene and n-butyl alcohol in the ratio of 9:1 so that the viscosity measured with a Ford cup No. 4 was 16 seconds. The paint thus prepared was sprayed onto a polystyrene plate and dried at 50°C for ten minutes to obtain a paint film about 10 microns thick. It was checked for peelproofness by the use of a cellophane adhesive tape, 15 mm wide, and by seeing if the pigment was not transferred to the tape when the latter was removed. This test is to check for the affinity between

the binder and the metallic pigment.

**TEST 5**  
(Shockproofness Test)

The paint film obtained in Test 4 was tested for shockproofness with a voltage tester. Voltage was applied to the paint film through electrodes spaced apart by 1 cm. It was increased from 1 kV to 6 kV in steps to check at what voltage an insulation breakdown occurred. The Table shows the maximum voltage applied without causing any breakdown.

**TEST 6**  
(Touchproofness Test)

10 The part of the aluminium pigment obtained in Example 8 was mixed with 35 parts of acryl lacquer (Acrylic A—165 of Japan Reichhold Chemicals Inc. NV 45%) and 62 parts of a solvent consisting of ethyl acetate, ethyl cellosolve and cyclohexane in the ratio of 40:30:30. The resulting metallic paint was sprayed onto a polystyrene plate and dried at 50°C for 20 minutes to prepare a metallic paint film about 10 microns thick. A finger was pressed onto the surface of the paint film and the film was then let to stand for ten days at 40°C and a relative humidity of 90%. Thereafter, the paint surface was examined for change.

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TABLE

	Control 1	Control 2	Ex. 1
Monomer A	—	—	EPPB 5.4g
Comonomer B	—	—	—
Al flakes (NV in wt. %)	HS-2 (72.0)	HS-2 (72.0)	1200M (65.0) 280g
Temp. x Time (hr)	—	—	70°C x 8H
NV (in wt. %) of Al pigment	—	—	70.3
Amount of coating (in wt. part)	—	—	0.4
Silicone compound (in wt. part)	—	SF-8411 1.5	—
NV (in wt. %) after mixing	72.0	72.5	55.3
Test 1	X	X	X
2 (in ml)	>20	>20	20
3	3.5	3.5	2.1
4	X	X	Δ
5 (in KV)	O	O	O
6	X	X	Δ

O: Good

X: Not usable

Δ: Not good but usable

TABLE (Continued)

	Ex. 2	Ex. 3	Ex. 4
Monomer A	EPPB 1.3g	EPPB 3.0g	EPPB 3.5g
Comonomer B	1,6— AA 2.2g 0.8g	1,6— AA 1.5g 0.9g	1,6— AA 5.1g 1.4g
Al flakes, (NV in wt. %)	HS-2 (72.0) 250g	MG-1000 (71.3) 250g	HS-2 (72.0) 250g
Temp. x Time (hr)	80°C x 6H	90°C x 4H	80°C x 6H
NV (in wt. %) of Al pigment	73.0	70.5	67.0
Amount of coating (in wt. part)	0.7	1.7	3.2
Silicone compound (in wt. part)	—	—	—
NV (in wt. %) after mixing	65.1	65.7	60.0
Test 1	X	O	O
2 (in ml)	5	2	0
3	1.4	1.3	0.5
4	0	0	0
5 (in KV)	1	2	4
6	Δ	Δ	Δ

O: Good

X: Not usable

Δ: Not good but usable

TABLE (Continued)

	Ex. 5	Ex. 6	Ex. 7	Ex. 8
Monomer A	GMA 6.5g	EPPB 12g	GA 56g	EPPB 1.3g
Comonomer B	1,6-AA 9.5g 2.5g	1,6-AA 12g 5g	—	1,6-AA 2.2g 0.8g
Al flakes (NV in wt. %)	MG-1000 (72.0) 250g	HS-2 (72.0) 250g	1200M (65.0) 280g	HS-2 (72.0) 250g
Temp. x Time (hr)	90°C x 4H	90°C x 4H	70°C x 8H	80°C x 6H
NV (in wt. %) of Al pigment	61.0	68.5	58.0	73.0
Amount of coating (in wt. part)	7.3	11.2	26.5	0.7
Silicone compound (in wt. part)	—	—	—	SF-8411 1.0
NV (in wt. %) after mixing	58.1	54.7	50.2	65.9
Test 1	O	O	O	X
2 (in ml)	0	0	0	—
3	0.5	0.2	0.3	1.6
4	O	O	O	O
5 (in KV)	>6	>6	>6	1
6	Δ	Δ	Δ	O

O: Good

X: Not usable

Δ: Not good but usable

## CLAIMS

1. A metallic pigment for paint, comprising metallic pigment particles coated with a polymer in the amount of 0.1 to 30 parts by weight per 100 parts by weight of the metallic component in the metallic pigment particles. 5

2. A metallic pigment as claimed in claim 1, wherein the metallic pigment particles are aluminium flakes. 10

3. A metallic pigment as claimed in claim 1 or 2, wherein the amount of the coating polymer is 0.5 to 15 parts by weight per 100 parts by weight of the metallic component in the metallic pigment. 10

4. A metallic pigment as claimed in claim 1, 2 or 3, including 0.5—5.4 parts by weight of a silicone compound per 100 parts by weight of non-volatile component in the polymer-coated metallic pigment. 15

5. A metallic pigment as claimed in claims 3 and 4, wherein the amount of the coating polymer is 0.5 to 3 parts by weight per 100 parts by weight of the metallic component in the metallic pigment. 15

6. A process for producing a metallic pigment for paint, comprising the steps of dissolving in an organic solvent, a monomer having a polymerizable double bond and at least one epoxy radical, or a mixture of said monomer and a comonomer having a polymerizable double bond, dispersing metallic pigment particles in said solution, and polymerizing said monomer, or said mixture at a temperature of 60—200°C in the presence of a polymerization initiator so as to coat said metallic pigment particles with the resulting polymer. 20

7. A process as claimed in claim 6, wherein the ratio by weight of the monomer to the comonomer is in the range from 3:10 to 10:10.

8. A process as claimed in claim 6 or 7, wherein the monomer is epoxidated polybutadiene and comonomers are 1,6-hexanedioldiacrylate and acrylic acid.

5 9. A process as claimed in claim 6, 7 or 8, wherein the metallic pigment particles are aluminium flakes.

10. A process as claimed in claim 6, 7, 8 or 9, including the step of adding to the polymer-coated metallic pigment 0.5 to 5.4 parts by weight of a silicone compound per 100 parts by weight of the non-volatile component in the polymer-coated metallic pigment.

10 11. A process as claimed in claim 10, wherein the silicone compound is silicone oil or silicone resin.

12. A process for producing a metallic pigment for paint, substantially as hereinbefore described.

13. A metallic pigment for paint, substantially as hereinbefore described.

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